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13. ABSTRACT (maximum 200 words) The objectives of this program are (1) to develop low voltage and high birefringence LC mixtures, (2) to develop negative dielectric anisotropic LC materials for high contrast display and wide-band infrared scene projectors, and (3) to deliver sample mixtures to device teams for testing. In the effort of developing high birefringence and low voltage LC mixtures for laser communications, we discovered some nitro-amino tolane dyes with very large dielectric anisotropy and relatively low viscosity. Adding 10% of this guest to the nonpolar diphenyl-diacetylene host, the threshold voltage drops from 4.0 to 1.5 V <sub>rms</sub> . In the meantime, these new compounds possess a relatively low viscosity so that they do not increase the response time too noticeably. In the effort of developing negative dielectric anisotropy LC compounds, we have designed and synthesized (collaborated with Chiao Tun University) several laterally fluorinated tolanes and diacetylenes. These LC compounds exhibit a large but negative dielectric anisotropy. They are useful for high contrast displays and for wide-band infrared scene projectors. We have delivered sample mixtures to Raytheon Lexington Labs, Kent State University, and MacroVision Communication for testing their laser beam steering, low voltage display and fiber-optic communications devices, respectively.				
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# **FAST RESPONSE LIQUID CRYSTALS FOR ELECTRO-OPTIC APPLICATIONS**

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## 1.0 INTRODUCTION

For laser communications using a liquid crystal (LC) optical phased array, the device should possess following features: (1) large scanning angle while keeping high diffraction efficiency, (2) fast scanning speed, (3) low optical loss, (4) low operation voltage and (5) wide operating temperature range. These system requirements translate into following desirable LC material parameters: (1) high birefringence ( $\Delta n$ ), (2) small visco-elastic coefficient ( $\gamma_1/K_{11}$ ), (3) small absorption loss, (4) large dielectric anisotropy ( $\Delta\epsilon$ ) and (5) wide nematic range.

In the previous AFOSR contract (F49620-92-C-0071), we have developed some asymmetric diphenyl-diacetylenic LCs. These compounds exhibit high  $\Delta n$ , low viscosity, wide nematic range and small heat fusion enthalpy. They are excellent host materials for laser communication applications. A drawback of these nonpolar compounds is their small dielectric anisotropy ( $\Delta\epsilon \sim 0.8$ ). The small dielectric anisotropy leads to a higher operation voltage. To improve dielectric anisotropy, we have investigated polar (e.g., fluoro and cyano) diphenyl-diacetylenes. Although these polar compounds do greatly enhance the dielectric anisotropy, their melting points are too high to be practically useful.

In the present program, we have explored a new approach that is to decouple the dipole moment from the linearly conjugated LC compounds. Our strategy is to design a guest compound with very large dielectric anisotropy and low viscosity and mix it with the nonpolar diphenyl-diacetylene host. Due to its huge dielectric anisotropy, we only need a small amount of this compound to see a dramatic reduction in the operation voltage. In the mean time, these new compounds possess a relatively low viscosity so that they do not cause much increase in viscosity to the mixture.

During this program, we have successfully: (1) developed nitro-amino tolane dyes with large dielectric anisotropy, (2) synthesized and evaluated lateral fluoro-tolanes and diacetylenes, (3) investigated IR absorption of LC compounds, and (4) delivered sample mixtures to Raytheon Lexington Labs, Kent State University, and MacroVision Communication, Inc. for device testings.

The nitro-amino tolane dyes we developed exhibit an extraordinarily large dielectric anisotropy, high  $\Delta n$  and relatively low viscosity. They are useful for reducing the threshold voltage of nonpolar diphenyl-diacetylene mixtures. These dyes are also attractive for lowering the operation voltage of polymer-stabilized cholesteric texture displays which are presently being developed in Kent State University. The laterally fluorinated tolanes and diacetylenes we developed in this

program exhibit a relatively large but negative dielectric anisotropy. These new LCs exhibit an excellent contrast ratio and are particularly useful for suppressing the noise level in fiber-optic communication currently developed by MacroVision, Colorado. In addition, we have identified low loss IR LC compounds. Several of our newly developed compounds show little absorption in the 4-5  $\mu\text{m}$  region. The commonly observed CN vibration band is eliminated. Two eutectic mixtures consisting of these low loss and high  $\Delta n$  LCs were delivered to Raytheon Lexington Labs for testing their beam steering devices.

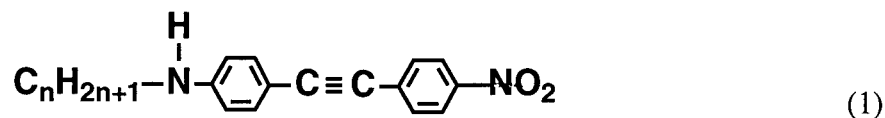
## **2.0 NEW LIQUID CRYSTAL MATERIALS**

During the course of this program, we have developed two types of new liquid crystal materials. The first type LC compounds possess a large and positive dielectric anisotropy while the second type has a negative dielectric anisotropy. The applications of these materials are quite different. For the positive materials, they can be added to an eutectic mixture to enhance the dielectric anisotropy and reduce the operation voltage of the mixture. Since the dielectric anisotropy of the new compounds is so large that we can just use a small fraction to achieve our goal without increasing the mixture viscosity too much. For an LC with a negative dielectric anisotropy, it is highly desirable for display application owing to its excellent contrast ratio. In this program, we have also synthesized several such LC compounds. These LCs possess a low melting point, large and negative dielectric anisotropy and high birefringence. As a result, they are useful for both display and IR modulator applications.

### **2.1. High Solubility Tolane Dyes**

Dyes with proper absorption wavelength, large dichroic ratio, high solubility and low viscosity are highly desirable for polarizer-free, liquid crystal guest-host displays. Absorption wavelength of a dye molecule is mainly determined by its molecular conjugation length. When dye molecules are dissolved in a LC host, its absorption wavelength may result in a red or blue shift depending on the detailed molecular interactions. Dichroic ratio makes important effects on the contrast ratio and brightness of the display device. Dichroic ratio of a dye is strongly affected by the molecular shape and interactions with host LCs. A linear dye molecule is expected to exhibit a larger dichroic ratio. The solubility of a dye molecule is determined mainly by its melting point and heat fusion enthalpy. Usually, a dye molecule may contain several phenyl rings and conjugated linking groups in order to obtain the desired color. As a result, its melting point is high ( $>100^\circ\text{C}$ ) and viscosity is large. Such dyes exhibit a very limited solubility ( $\sim 2\%$ ) and huge viscosity. A poor solubility implies that a thicker LC layer is needed in order to obtain good contrast ratio which results in a slower response time. On the other hand, the observed large viscosity originates from the large moment of inertia of these elongated dye molecules.

The structures of the amino-nitro biphenyl azo and tolane dyes we studied are shown below:



where  $n$  represents the number of side-chain carbon atoms. For simplicity, the tolane dyes are abbreviated as  $n\text{NH-PTP-NO}_2$ ; here P stands for a phenyl ring, N for nitrogen, and T for the carbon-carbon triple bond.

We have synthesized four tolane dyes with  $n=4-7$ . Their  $[T_m, \Delta H]$  were measured to be: [119.3, 6.27], [98.3, 4.69], [93.4, 8.82], and [87.5, 6.29], respectively. Unlike the azo dyes, these tolane dyes exhibit no mesogenic phase. As the side chain length increases, the melting point gradually decreases. The odd-even effect on the transition temperature is not clearly observed. Among the compounds we studied, the  $n=5$  homologue exhibits the lowest heat fusion enthalpy. Thus, its solubility should be the highest. The more linear structure of the tolane dyes should possess a slightly lower viscosity and higher dichroic ratio than the corresponding azo dyes.

Absorption wavelength, dichroic ratio, dielectric anisotropy, solubility, viscosity and birefringence of some nitro-amino tolane and azo dye molecules were studied. Results are discussed as follows.

### 2.1.1. Dichroic Ratio

Polarized absorption spectra and dichroic ratio of several dyes (1% concentration) were measured in the E63 and ZLI-4792 LC hosts (from Merck). Results are listed in Table I.

Table I Absorption wavelength ( $\lambda_{\text{max}}$  in nm) and dichroic ratio (DR) of some nitro-amino tolane (PTP) and azo (PNNP) dyes in host E63 and ZLI-4792.  $T=22^\circ\text{C}$ .

Dyes	DR ( $\lambda_{\text{max}}$ ) in E63	DR ( $\lambda_{\text{max}}$ ) in ZLI-4792
1. 5NH-PTP-NO <sub>2</sub>	7.8 (417)	7.4 (401)
2. 5NH-PNNP-NO <sub>2</sub>	6.7 (477)	7.3 (451)
3. 7NH-PNNP-NO <sub>2</sub>	6.9 (476)	
4. 9NH-PNNP-NO <sub>2</sub>	7.6 (478)	
5. 11NH-PNNP-NO <sub>2</sub>	7.6 (477)	
6. 5NCH <sub>3</sub> -PNNP-NO <sub>2</sub>	6.0 (498)	6.5 (485)
7. 6NCH <sub>3</sub> -PNNP-NO <sub>2</sub>	6.2 (498)	
8. SI-209 (commercial)	6.9 (450)	



From Table I, the absorption peak of the tolane dye in E63 occurs at 417 nm with dichroic ratio 7.8. Replacing the acetylene by an azo linking group causes a significant red shift (477 nm) and decreased dichroic ratio (6.7). This is because the molecular conjugation of the azo group slightly tilts away from the principal molecular axis. For the homologous with different side chain length, their  $\lambda_{\max}$  remains basically unchanged. However, the dichroic ratio slightly increases and then saturates as the chain length increases. Simply replacing the NH group by a NCH<sub>3</sub>, its  $\lambda_{\max}$  shifts toward red by ~ 20 nm. The trade off is in the reduced dichroic ratio. A commercial dye SI-209 (an azo methane derivative; from Mitsui Toatsu Chemicals) is also listed here for comparison. Host ZLI-4792 is a high resistivity, low  $\Delta n$  mixture developed for active matrix LC displays. It is less polar than E63 (mainly cyano-biphenyls). Thus, the  $\lambda_{\max}$  in ZLI-4792 is shorter than that in E63. The dichroic ratio varies slightly among these two hosts.

### 2.1.2. Birefringence

Birefringence, threshold voltage ( $V_{th}$ ), dielectric anisotropy and visco-elastic coefficient ( $\gamma_1/K_{11}$ ) of the guest-host systems were measured. The effect of 5NH-PTP-NO<sub>2</sub> dye on the  $\Delta n$  and  $V_{th}$  of E63 is shown in Fig.1. In general, under the same wavelength and same reduced temperature ( $T_R$ ),  $\Delta n$  of a guest-host system can be approximated by:  $\Delta n_{gh} = x_g \Delta n_g + x_h \Delta n_h$ ; where  $x_{g,h}$  (with  $x_g + x_h = 1$ ) and  $\Delta n_{g,h}$  are the concentration and  $\Delta n$  of the guest and host, respectively. From Fig.1, the  $\Delta n$  of the tolane dye is extrapolated to be 0.42 at  $T_R = 0.821$  and  $\lambda = 633$  nm.

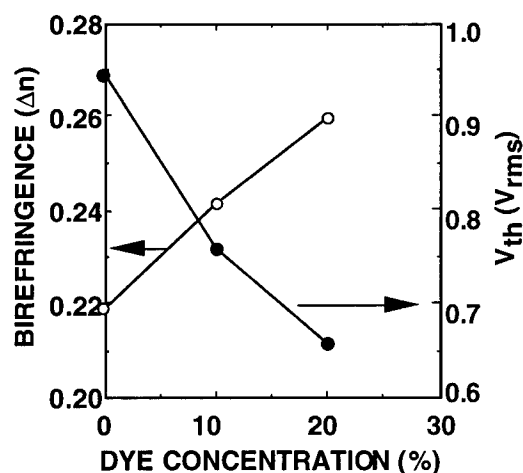


Fig. 1 Dye concentration effect on  $\Delta n$  (open circles) and  $V_{th}$  (filled circles). Dye=C5 tolane; LC host = E63.  $T=22^\circ\text{C}$  and  $\lambda=633$  nm.

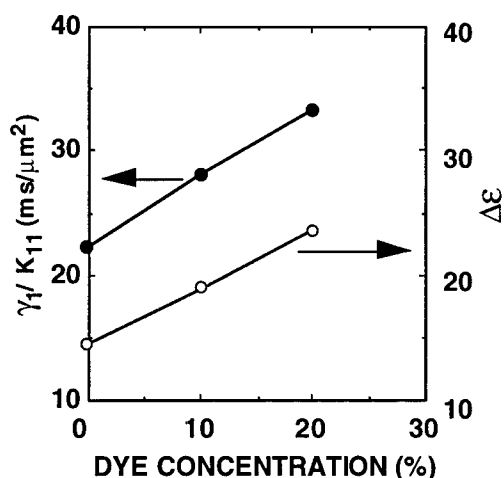


Fig.2 Dye concentration effect on  $\Delta\epsilon$  (right) and  $\gamma_1/K_{11}$  (left). Dye=C5 tolane, LC host=E63.  $T=22^\circ\text{C}$ .

### 2.1.3 Dielectric Anisotropy

The decreasing  $V_{th}$  implies that the  $\Delta\epsilon$  of 5NH-PTP- $NO_2$  dye is larger than that of E63. Nevertheless, this drop is not linear because  $V_{th} (= \pi\sqrt{K_{11} / \Delta\epsilon})$  is not linearly dependent on  $\Delta\epsilon$ . To estimate the  $\Delta\epsilon$  of the dye, we measured the dielectric constants of the guest-host mixture at different dye concentration. Results are shown in the right-hand side of Fig.2. From these data,  $\Delta\epsilon$  of the C5 tolane dye is extrapolated to be  $\sim 60$  at  $T_R = 0.821$ .

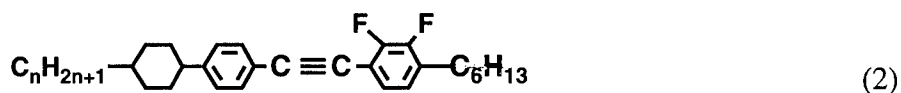
### 2.1.4 Viscosity

On the left-hand side, the concentration effect on the visco-elastic coefficient is depicted. Again, as the dye concentration increases, the  $\gamma_1/K_{11}$  of the guest-host system increases linearly. However, this increase is considered small as compared to some commercial dyes, such as the anthraquinone type (Merck). From Fig.2, adding 10% of the tolane dye to E63 LC host merely increases  $\gamma_1/K_{11}$  by 25% which is about one order of magnitude smaller than that of 1% anthraquinone dye in the same host.

The large  $\Delta\epsilon$  of these LC dyes results from their extraordinarily strong dipole moment originating from the amino-nitro intramolecular charge transfer. The  $NO_2$  group acts as an acceptor that induces electron flow from the benzene ring. On the other hand, the  $(C_nH_{2n+1})NH$  group acts as an electron donor which produces an opposite charge flow.

## 2.2 (2,3) Difluoro Tolanes and Diphenyl-Diacetylenes

The structures of the laterally difluorinated tolanes we studied are shown below:



We have synthesized several homologues with  $n=2-7$ . Similar tolanes with alkoxy side chains have been reported by Merck group. These alkoxy tolanes possess high melting point and large heat fusion enthalpy. Thus, their solubility in a LC mixture is limited even though their high clearing point ( $T_c$ ) is attractive for enhancing the  $T_c$  of the mixture.

### 2.2.1. Phase Transition Temperatures

The phase transition temperatures and heat fusion enthalpy ( $\Delta H$ ) of the (2,3) difluoro-tolanes we designed and synthesized (by Prof. Hsu's group of National Chiao Tung University) are listed in Table II.

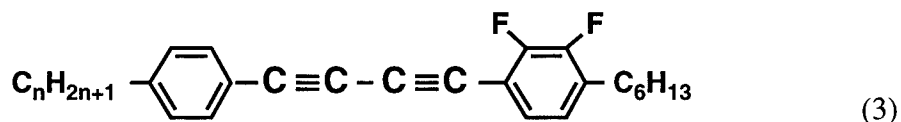
TABLE II Phase transition temperatures (in  $^{\circ}\text{C}$ ) and heat fusion enthalpy ( $\Delta H$  in kcal/mol) of the laterally difluoro-tolane LC homologues. Here K, N and I stand for crystalline, nematic and isotropic phase, respectively.

n	Phase transitions					$\Delta H$
2	K	34.6	N	75.9	I	3.52
3	K	38.5	N	94.2	I	2.28
4	K	22.5	N	105.8	I	3.05
5	K	38.3	N	104.6	I	5.22
6	K	36.8	N	68.9	I	2.60
7	K	37.2	N	86.2	I	2.85

These homologues exhibit relatively low melting temperatures and high clearing point. Normally, the asymmetric side chain groups help to reduce melting temperature. However, this phenomenon is not so obvious here. The observed low melting temperature is mainly attributed to the molecular width. The lateral difluoro group widens the molecular separation and weakens the inter-molecular association resulting in low melting temperatures. On the other hand, the high clearing temperature originates from the cyclohexane ring. The small  $\Delta H$  of these homologues is quite desirable for forming eutectic mixtures. According to the Schroder-Van Laar equation, both low melting temperature and small heat fusion enthalpy play equally important roles in reducing the melting temperature of an eutectic mixture. Low melting temperature and high clearing point are critical for practical display applications. Normally, the desirable nematic range of a LC mixture is from  $-40$  to  $+85^{\circ}\text{C}$ .

### 2.2.2. (2,3) Difluoro Diphenyl-Diacetylenes

The structure of the (2,3) laterally difluorinated diphenyl-diacetylene liquid crystals we studied is shown below:



The compounds we synthesized have  $n=3-6$ . Their phase transition temperatures and heat fusion enthalpy are listed in Table III. Normally, the melting temperature of such a highly conjugated liquid crystal would be quite high. However, due to the lateral substitutions, their melting point is reduced to near room temperature.

The physical properties of the  $n=4$  homologue was characterized and results are included in Table III. The high  $\Delta n$  results from long molecular conjugation and the large negative dielectric anisotropy from lateral dipole moment.

TABLE III Phase transition temperatures (in  $^{\circ}\text{C}$ ), dielectric anisotropy ( $\Delta\epsilon$  at  $T=25^{\circ}\text{C}$  and 1 kHz), birefringence ( $\Delta n$  at  $\lambda=633$  nm) and heat fusion enthalpy ( $\Delta H$  in kcal/mol) of the laterally difluoro diphenyl-diacetylene LC homologues. Here K, N and I stand for crystalline, nematic and isotropic phase, respectively.

n	Phase transitions	$\Delta\epsilon$	$\Delta n$	$\Delta H$
3	K 37.5 N 71.1 I			4.13
4	K 23.6 N 47.2 I	- 6.4	0.28	4.25
5	K 34.6 N 58.7 I			4.46
6	K 19.6 I			---

The absorption edge of the diphenyl-diacetylene LCs extends to 350 nm. Thus, their photostability in the blue spectral region is a concern and not so desirable for visible display application. However, there are other displays or light modulation in the infrared and microwave regions where photostability of these LCs is not a problem as long as the cell is sealed. To improve the lifetime of a LC device, the cell should be sealed peripherally in order to keep moistures and oxygen out. Otherwise, moistures and oxygen tend to interact with LC molecules and cause alignment deterioration. As a result, the contrast ratio of the LC device is degraded gradually. The high birefringence and negative dielectric anisotropy of these compounds turn out to be attractive for such applications.

### 3.0 IR ABSORPTION OF LIQUID CRYSTALS

Absorption has great impact on the transmittance of a LC device. In the IR region, there are several fundamental molecular vibrational bands, such as C-H, C-C, C-O, C=C and C≡N exist in the IR region. The detailed molecular vibration frequency ( $\omega$ ) depends on the reduced molecular weight ( $m$ ) and its spring constant ( $\kappa$ ) as  $\omega = (\kappa/m)^{1/2}$ . For a broad band (e.g., 3-5, 8-12  $\mu\text{m}$ ) operation of an LC filter, some optical loss which originates from the molecular vibration absorption is unavoidable. Nevertheless, if the application only involves a designated laser line, the absorption loss may be minimized by carefully choosing proper LC compounds.

We have selected 5 LC compounds which have been frequently used in the mixtures and then measured their absorption in the 2.5 to 20  $\mu\text{m}$  range. These compounds are cyano-biphenyl (5CB), isothiocyanate (PCH-3S), fluoro-tolane (PTP-6F), asymmetric dialkyl diphenyl-diacetylene (PTTP-15) and fluoro diphenyl-diacetylene (PTTP-6F). Because the melting temperature of some compounds is relatively high, we studied the IR spectra as 1% solutions of each compound (except for 5CB) in the methylene chloride ( $\text{CH}_2\text{Cl}_2$ ) solution. Two 1-cm-thick LC cells with KCl substrates were used for all the measurements. The normalized transmission of the sample cell was measured against a reference cell containing only methylene chloride. Due to different amount of methylene chloride present in each cell, the data shown below only represent a relative transmittance of the LC sample. However, in 5CB, it is liquid at room temperature. We measured its transmission using a homogeneous-aligned cell against a KCl substrate. Therefore, the measured data represents a normalized transmittance.

#### 3.1. 5CB

The structure of the 5CB LC compound is shown below:



Figure 3 shows the normalized transmittance spectrum of a 4- $\mu\text{m}$ -thick 5CB cell. The seven bands numbered in Fig.3 are: 1) the C-H stretching vibration located at 3.44  $\mu\text{m}$ , 2) the CN stretching vibration located at 4.45  $\mu\text{m}$ , 3) and 4) the C=C skeletal in-plane deformations in benzene located at 6.25 and 6.71  $\mu\text{m}$ , respectively, 5) the C-H in-plane deformation located at 8.45  $\mu\text{m}$ , 6) the C-C in-plane deformation located at 9.95  $\mu\text{m}$ , and 7) the C-H out-of-plane deformation located at 12.32  $\mu\text{m}$ . The CH,  $\text{CH}_2$  and  $\text{CH}_3$  vibrational bands are superimposed in the 3.2 to 3.8  $\mu\text{m}$  region. Their transition intensities are rather strong. These hydrocarbon associated vibration absorption are

intrinsic to nearly all the thermotropic LC molecules discovered so far. Thus, all the LC tunable filters will suffer huge absorption loss in this region.

Also present in the 3-5  $\mu\text{m}$  mid-IR band is the well-known  $\text{C}\equiv\text{N}$  terminal group. The  $\text{C}\equiv\text{N}$  group exhibits a large dipole moment so that the operation voltage of the LC is low. However, its vibration occurs at 4.45  $\mu\text{m}$  and its absorption is quite strong. For a tunable filter operating in the 3-5  $\mu\text{m}$  band, it is highly desirable to eliminate the CN absorption band. Fortunately, not every LC compound contains a CN group. We have found some fluoro tolans and diphenyl-diacetylenes possessing a modest dipole while significantly reducing the absorption in the vicinity of 4.5- $\mu\text{m}$ .

In the 8-12  $\mu\text{m}$  (or 1250-833  $\text{cm}^{-1}$ ) region, bands 5, 6 and a portion of 7 exist. These bands are also intrinsic to all the thermotropic liquid crystals discovered so far. Thus, tailoring a highly transparent LC mixture for the 8-12  $\mu\text{m}$  band is a difficult task. Since the absorption loss is related to  $\alpha d$ , besides looking for a more transparent LC mixture, a simple way for reducing absorption loss is to use a high  $\Delta n$  material so that the LC layer thickness is minimized.

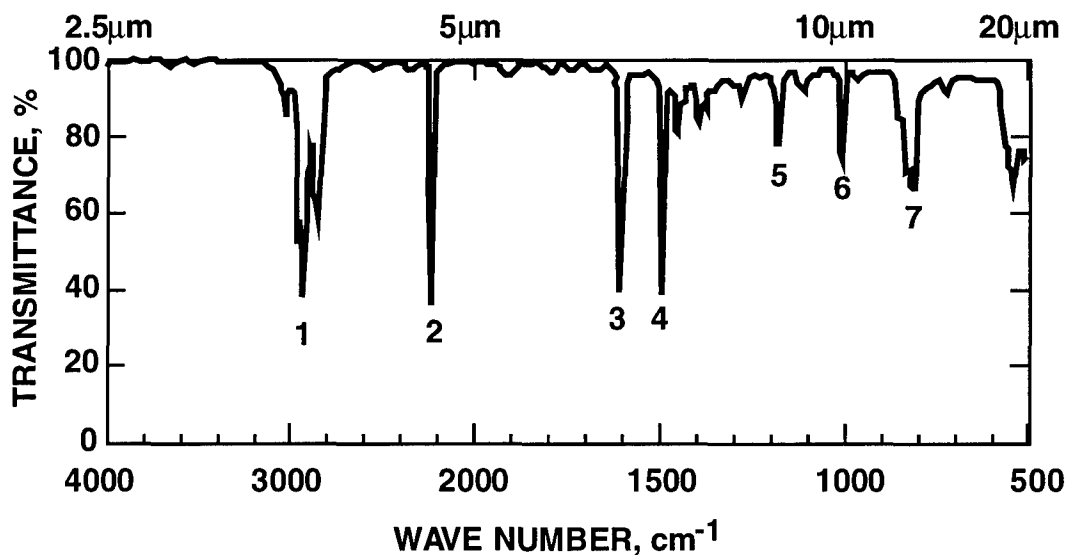


Fig.3 Normalized transmittance of 4- $\mu\text{m}$ -thick 5CB layer at  $T=23^\circ\text{C}$ . The numbered absorption bands are discussed in the text.

### 3.2. PCH-3S

The structure of the PCH-3S LC compound is shown below:



The isocyanate (NCS) group is known to exhibit a large dipole moment while retaining a lower viscosity and higher birefringence than the corresponding cyano compound. However, as shown in Fig.4, its absorption is strong and spans over a wide range (4.3 - 5.3 and 10.3 - 11.2  $\mu\text{m}$ ). This makes NCS group undesirable for the 3-5 and 8-12  $\mu\text{m}$  bands operation.

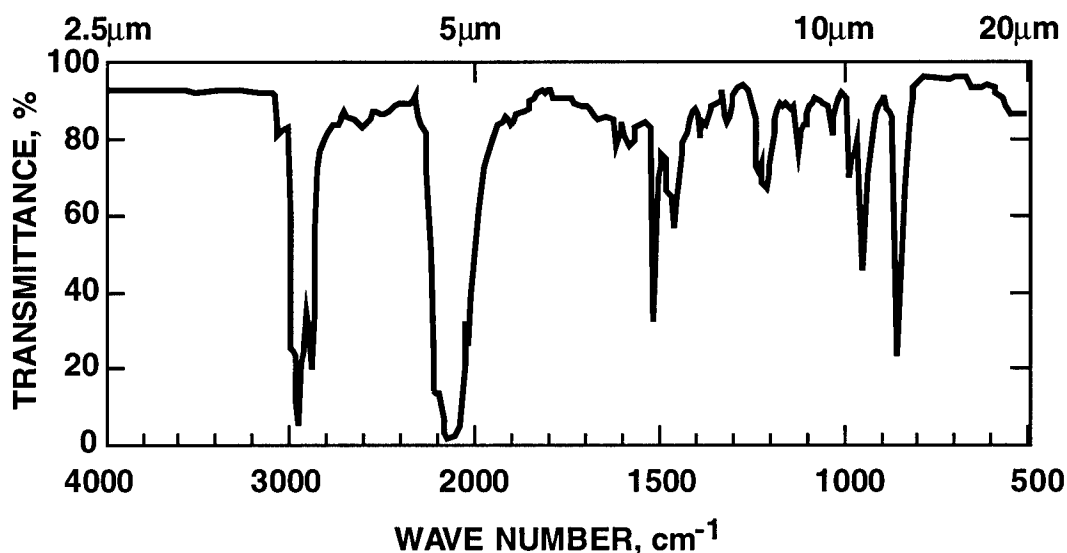


Fig.4 Relative transmission spectrum of 1% PCH-3S dissolved in methylene chloride solution. Cell thickness: 1 cm,  $T=23^\circ\text{C}$ .

### 3.3. PTP-6F

The molecular structure of the PTP-6F compound is shown below:



The reduced mass of  $\text{C}\equiv\text{C}$  only differs slightly from  $\text{C}\equiv\text{N}$  so that its vibration wavelength also occurs in the vicinity of 4.5- $\mu\text{m}$ . Unlike the cyano group whose stretching vibration is sharp and its intensity is strong, the acetylene exhibits a much weaker transition intensity, as shown in Fig.5. The cyano-tolane possesses a higher  $\Delta n$  than the corresponding fluoro-tolane. However, its viscosity is also higher. Thus, fluoro tolane is still a potential candidate for mid-IR application.

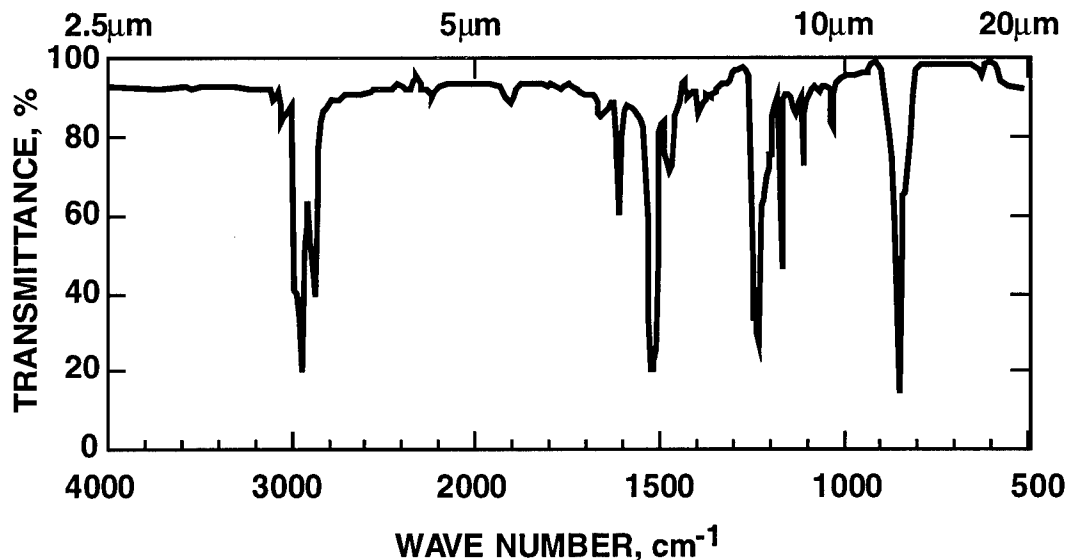
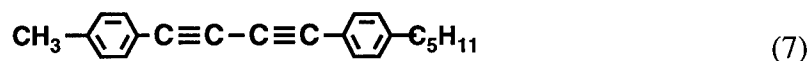


Fig.5 Relative transmission spectrum of 1% PTP-6F dissolved in methylene chloride solution. Cell thickness: 1 cm,  $T=23^{\circ}\text{C}$ .

### 3.4. PTTP-15

The molecular structure of the PTTP-15 LC compound is shown below:



The dialkyl diphenyl-diacetylene LCs exhibit large birefringence, low melting point and wide nematic range, small heat of fusion and low viscosity. They are excellent host materials for formulating LC mixtures with wide nematic range. Merely mixing four PTTP homologues together, the mixture exhibits a melting temperature below  $-10^{\circ}\text{C}$  and the clearing temperature above  $90^{\circ}\text{C}$ . A disadvantage of these compounds is in their small dielectric anisotropy ( $\Delta\epsilon=0.8$ ) due to the relatively symmetric structure.

Figure 6 depicts the relative transmission spectrum of PTTP-15 dissolved in methylene chloride solution. The diacetylene ( $\text{C}\equiv\text{C}$ )<sub>2</sub> linking group exhibits two vibration transitions (one at  $4.54$  and another at  $4.66\text{ }\mu\text{m}$ ); both have a relatively low intensity. Thus, PTTP homologues are quite attractive for mid-IR applications.



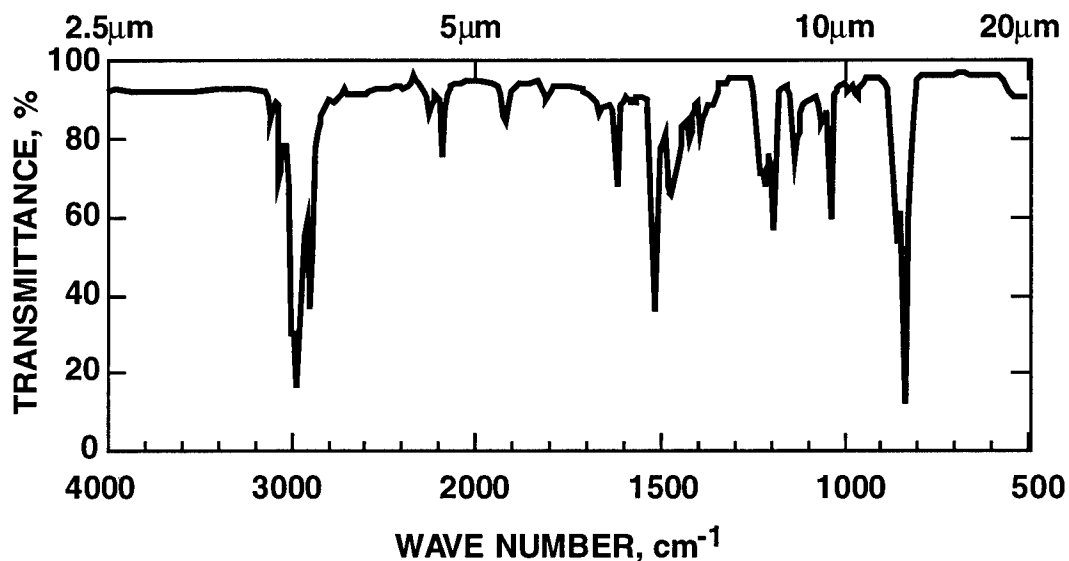
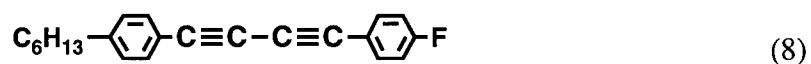


Fig.6 Relative transmission spectrum of 1% PTTP-15 dissolved in methylene chloride solution. Cell thickness: 1 cm, T=23°C.

### 3.5. PTTP-6F

The molecular structure of the PTTP-6F LC compound is shown below:



The fluoro group enhances dielectric anisotropy to ~5. This compound has a few degrees of nematic range (76-80°C). It can be doped to nonpolar PTTP mixtures for reducing their operation voltage. Figure 7 shows the transmission spectrum of PTTP-6F. Its absorption characteristics are rather similar to those of dialkyl PTTP-15 shown in Fig.6.

Although the fluorinated PTTP homologues show a much smaller absorption over the cyano compounds in the vicinity of 4.5 μm, their overall absorption characteristics in the 8-12 μm region are not improved noticeably. However, for the 10.6-μm laser line, the PTTP-6F does show a lower absorption than the cyano compounds.

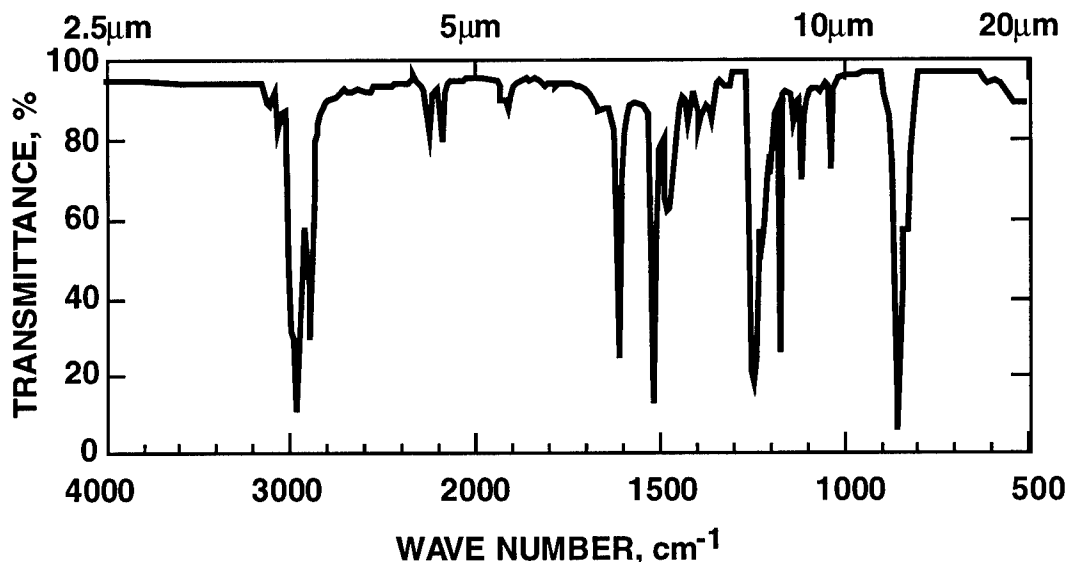


Fig.7 Relative transmission spectrum of 1% PTPP-6F dissolved in methylene chloride solution. Cell thickness: 1 cm,  $T=23^{\circ}\text{C}$ .

#### 4.0 SAMPLE DELIVERY

During the course of this AFOSR contract (F49620-94-C-0078), we have delivered high birefringence LC sample mixtures to Kent State University in the first year, MacroVision Communication in the second year, and Raytheon Lexington Lab. in the third year.

In addition, the following companies or research institutes have requested similar diphenyl-diacetylene mixtures through Dr. Mary Neubert of Kent State University:

1. Boulder Nonlinear Optics (Colorado)
2. MacroVision Communication (Colorado)
3. Meadowlark Optics (Colorado)
4. JPL NASA (California)
5. Universite de Montpellier II (France)

## 5.0 SUMMARY

The asymmetric diphenyl-diacetylenes we developed in the previous AFOSR contract exhibit a low melting temperature, wide nematic range, high birefringence, small heat fusion enthalpy and low viscosity. They are excellent host materials for formulating eutectic mixtures for laser beam steering application. However, the dielectric anisotropy of these nonpolar compounds is too small. Some polar diphenyl-diacetylene liquid crystals have been studied. Although the dielectric anisotropy has been enhanced, the melting point of these polar compounds are too high to be practically useful.

Our strategy is to decouple the dipole moment from a linearly conjugated LC compound. We have investigated nitro-amino tolane dyes. Owing to the push-pull effect, the dielectric anisotropy of these linearly conjugated tolanes is about 60. Adding 10% of this component to diphenyl-diacetylene mixture reduces the threshold voltage from 4 to 1.5 volts. On the other hand, the viscosity of such mixture only increases by about 25% which is about one order magnitude lower than the commercial anthraquinone dye in the same host.

We have also studied some laterally-fluorinated tolane and diphenyl-diacetylene liquid crystals for display applications. These LCs possess a relatively large but negative (-6) dielectric anisotropy. Moreover, the melting points of these (2,3) difluoro compounds are close to room temperature. Plus small heat fusion enthalpy, these compounds are very attractive for high contrast displays employing homeotropic alignment. A problem associated with homeotropic alignment is that its viewing angle is rather limited. We have developed several methods for widening its view angle.

Another big concern of IR laser communication using liquid crystal as light modulation medium is absorption. We have investigated the absorption mechanisms of liquid crystals in the infrared region. In the IR region, there are several fundamental molecular vibrational bands, such as C-H, C-C, C-O, C=C and C $\equiv$ N exist in the IR region. The detailed molecular vibration frequency ( $\omega$ ) depends on the reduced molecular weight ( $m$ ) and spring constant ( $\kappa$ ) as  $\omega = (\kappa/m)^{1/2}$ . For a broad band (e.g., 3-5, 8-12  $\mu$ m) operation of an LC modulator, some optical loss which originates from the molecular vibration absorption is unavoidable. Nevertheless, if the application only involves a designated laser line, the absorption loss may be minimized by carefully choosing proper LC compounds.

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